

Limestone-filled, hydraulic-lime mortars for historic and traditional fabrics.

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Abstract

Hydraulic lime (HL) mortars are considered compatible with historic fabrics and used in repairs. They consist of lime and clinkers (mainly belite). As belite hydrates slowly, some HLs develop strength for up to a year. This has raised concerns with conservationists. This paper partially replaces natural HL (NHL5) with limestone to lower ultimate strengths that can damage for some fabrics. It investigates the hydration of NHL5 in the presence of limestone and the impact on mortar properties.

Despite the NHL's low aluminate content, limestone reaction is evident. Limestone-triggered hydrates appear in the matrix and at interfaces, likely strengthening the transition zone. The limestone fineness and permeability, and the significant specific surface area of its microcrystalline carbonate may have enhanced reactivity.

The 10-20% limestone replacements increased the 28-day strength. However, they lowered the NHL5 strength after 90 days (flexural) and 180 days (compressive). In contrast, the NHL5 mortar keeps developing compressive strength, increasing by c.14 between 90 and 180 days and c. 10% between 180 days and 1 year. The strength raise did not significantly affect the hygric properties. When NHL5 is replaced with 10-30% limestone, the finest mortar pores are preserved (water vapour permeability varies insignificantly). Contrary to Portland cement (PC), the limestone lowers the water demand of the NHL5 mortars. To achieve a proper workability using less water has benefits relevant for those involved in mortar design.

Introduction

Limestone is considered an active addition in PC and currently, the European Standards [1] include four limestone cements with limestone content ranging from 6 to 35%. In the cement industry, limestone has been linked to lower costs, enhanced performance, energy saving and reduction of CO₂ emissions on cement production [2-4]. Hydraulic limes (HLs) contain silicate and aluminate clinkers identical to those in PC however, limestone is not added to HL. Natural hydraulic limes (NHLs) have been used since antiquity. Today NHL mortars are considered masonry-compatible due to their hygric and mechanical properties [5-14] and are used in new building and masonry repair. They

are regaining popularity as a more sustainable alternative to PC because they require lower production energy and absorb part of their CO₂ emissions during hardening. Their chemical and physical compatibility relies on the fact that they contain a mixture of free lime and aluminate and silicate clinkers (of which belite-C₂S- is the most abundant). The free lime provides workability and sustained plasticity due to its high water retention, while the belite delivers hydraulic cements that contribute to strength gain and enhance durability. This results in materials of high water vapour permeability, lower strength and a greater plasticity than cement-based materials which have been favoured in restoration for decades. It is known that NHL mortars display bond strengths and structural behaviour compatible with masonry units; and that the hydraulic set of NHLs leads to earlier strength development and a greater ultimate strength, a lower shrinkage and a superior durability than hydrated limes [5-14]. European designation HL5/NHL5 (with the greatest hydraulic content) is used when a fast set and hardening and a greater durability are required (strong exposure or presence of water). Per standard requirement, HL5/NHL5 must reach over 7 N/mm² at 28 days [15], however, there is no long-term strength requirement in the standards. Belite hydrates so slowly that the strength of NHL5-based materials will keep rising after 28 days and well after the material has been set into the fabric. This has raised concerns within conservationists as, in practice, a HL5/NHL5 mortar can develop strength for up to a year and after. This paper reviews the effect of limestone in PC and experimentally investigates limestone impact in HL using a NHL5 complying with EN459-1 [15], including 15-22% available lime and significant (43%) belite.

Limestone in PC

Influence of limestone on PC hydration

By 1938, Bessey [16] had already suggested that ground limestone takes part in reactions with PC aluminates. Later, other authors evidenced that carbonate ions (CO₃²⁻) replace sulfate ions (SO₄²⁻) in cement hydrates so that calcium carboaluminate forms in place of monosulfate – AFm phases- [17-21]. According to these authors, C₃A hydrates into C₃A. 1/2CO₂. 12H₂O which reacts with CO₃²⁻ resulting from limestone dissolution to form calcium carboaluminate hydrate (C₃A. CaCO₃.11H₂O). This phase, growing epitaxially on CaCO₃, was observed by Barriochini and Murat [22] and others. The reaction of alite with CaCO₃ to form calcium carbosilicate which leads to an early strength increase has been reported by Pera et al. [23]. Authors also report that limestone (CaCO₃) accelerates PC hydration [23-27], in particular the hydration of alite. The acceleration is attributed to CaCO₃ particles acting as nuclei for the formation and growth of more abundant C-S-H and CH which causes a drop in the concentration of Ca and Si ions in the interstitial solution that speeds up clinker dissolution.

Impact of limestone on PC properties

In PC, limestone increases water demand [23] and increases early strength. The early strength increase has been attributed to speeding up hydration and to the resulting calcium carbo-silicate and calcium carboaluminat hydrates improving density. Low level limestone replacements (5-10%) either not reduce or increase strength but a dilution effect exists at higher dosages unless the cement is ground finer to compensate [23-26]. Livesey [28] reports that 5% limestone replacement accelerates strength gain at early ages. Vuk et al.[29] report early strength increase with 5% limestone however, later strength either remained the same or decreased depending on the clinker fineness and chemistry. At higher limestone replacements (15-25% and over) strengths are lower than for comparable PC mixes [30-31]. The greater packing of the granular skeleton caused by fillers that lifts strength is well known [25]. This effect is apparent at early ages but does not produce additional ultimate strength [32]. Most authors claim that the calcium carbo-silicate hydrates (resulting from the limestone/ alite reaction) increase strength however, there is no agreement on the strength increase by the calcium carboaluminat hydrates (from the limestone/C₃A reaction). Some authors [23-25] state that they barely increase strength while others [2, 33-34] claim that they contribute to the early strength, because they are stiffer and have greater molar volume than the corresponding sulfoaluminates (AFm) and final cubic hydrates (C₃AH₆) that would result from the hydration of C₃A alone.

Materials and methods

The limestone qualifies as a filler (both in composition and grading). It consists of 95.8% CaCO₃ and practically no clay (Al₂O₃=0.3% by weight) -table 1- therefore, it qualifies as a filler [35-36]. According to the particle size distribution (figure 1), c.63% of the limestone is graded under 0.063 mm thus qualifying as a filler according to EN 933-10 [37]. It is widely acknowledged that fine limestone filler (with a greater specific surface area) enhances formation and growth of C-S-H and the dissolution of CaCO₃ to generate CO₃²⁻ thus accelerating and amplifying silicate and aluminat reactions.

Table 1. Composition (% by mass) and properties of the Portland stone base bed [36].

Ca CO ₃	Mg carbonates	Alumino silicates	Fe ₂ O ₃	SiO ₂	Water+ other	Porosity %	Capillary suction g/m ² .s ^{0/5}	%Water absorption
95.8	1.2	0.3	0.3	1.3	1.4	15.40	82.16	7.19

The limestone filler was chosen with a view to enhance the compatibility of the NHL repair mortars with the substrate. The limestone used to make the filler features in many, 18th century buildings in Dublin including the Four Courts (1775) (figure 2) which often show old mortar repairs made with crushed Portland stone (figure 3). It is an oolitic limestone consisting of calcite (CaCO₃) with traces of silica in the form of quartz (SiO₂). It contains abundant microcrystalline CaCO₃, with a higher specific surface and a greater

reactivity than coarser, crystalline carbonates. It has a grain supported fabric of ooids (figure 4), with substantial inter-particle space which results in significant porosity and permeability (table 1). Macropores (10–100µm) dominate the pore system and c. 20% micropores (0.01-0.20 µm) are also present [36].

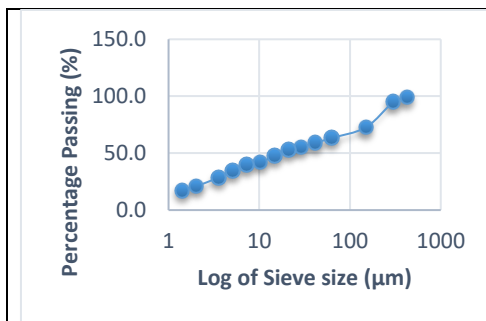


Figure 1. Particle size distribution of the limestone filler.



Figure 2. Portland stone at The Four Courts showing old mortar repairs made with crushed Portland stone - figure 3.

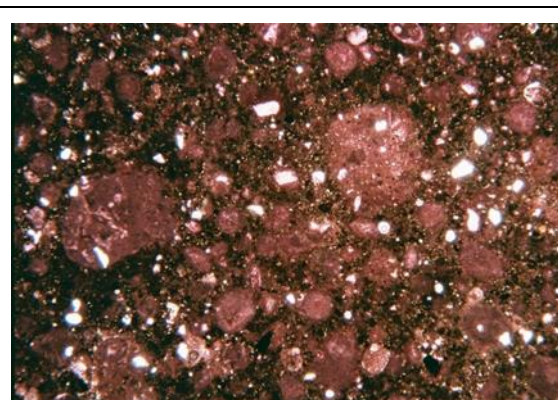


Figure 3. Petrographic photograph of an early 20th century repair mortar made with crushed Portland stone and fine quartz sand set a PC binder. 2X natural light. Field of view c. 7 mm.

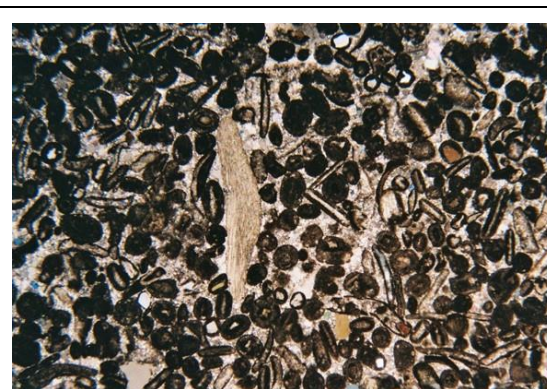


Figure 4. Petrographic image of the Portland stone consisting of ooliths and shells of microcrystalline carbonate cemented with coarser crystalline carbonate. 2X polarised light. Field of view c. 7 mm

The NHL5 contains available lime – $\text{Ca}(\text{OH})_2$ - (15-22% after slaking), residual unburnt CaCO_3 (23%) and significant belite (43% - C_2S) -table 2. Some C_3S –alite- can be present due to “high-temperature spots” during burning. The NHL5 has no impurities relevant to classification and labelling and a minimal presence of Al_2O_3 (up to c. 2%) sulphates and alkalis, which are very low in the parent limestone (table 2). The XRD analysis evidenced significant CH (Portlandite – $\text{Ca}(\text{OH})_2$), silicates (alite/belite) and some carbonate (CaCO_3), silica (SiO_2) and lime (CaO). The peaks identified as alite (Ca_3SiO_5) correspond to both belite and alite. It was not possible to tell them apart as the most intense peaks of belite are overlapped by alite and the alite content is likely under the detection limit. The surface area of the NHL5 is 8000 cm^2 per gram [38].

Table 2. Chemical and mineral composition of the NHL5 in % by mass [38].

Chemical composition									
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O/Na ₂ O	LOI	CaO ₂ - calcimetry	Insoluble
59	15	1.92	0.57	0.41	1.01	0.28	16	10	5.6
Mineral composition									
Ca(OH) ₂	Ca CO ₃	C ₂ S	C ₃ A	C ₂ AS	C ₄ AF	CaSO ₄			
22	23	43	0.7	1.3	0.7	0.7			

Mortar composition and curing. Mortars with NHL5 binder replaced with limestone (10, 20 and 30% by weight) were produced with a binder/aggregate ratio of 1:3 by weight. The aggregate is a siliceous sand similar to the CEN standard sand-Table 3. Workability and aggregate content were kept constant to attribute the variation of properties to the limestone content. All mortars were mixed to a 165±5 mm initial flow in order to measure how the limestone filler affects workability and the mortar's water demand to reach a specific flow. The 165±5 mm flow was selected because it provided the best workability by trial [39]. The results evidenced that, despite the considerable porosity of the limestone filler, increasing limestone content lowered the water demand of the NHL5 mortars -Table 3. On the contrary limestone replacement increases the water demand of PC composites [23]. The mortars were moulded and compacted on a vibration table according to EN 459-2 [39]. They were cured for 25 days at 90% humidity and 20 ± 2°C temperature. After 28 days, some specimens were tested and the rest kept in standard conditions for testing at 90 and 180 days. Each property measured is the arithmetic mean of six specimens.

Table 3. Composition and water content of the mortars.

Designation	% NHL5	% Limestone	W/B
100% NHL5	100	0	0.73
10% L	90	10	0.69
20% L	80	20	0.64
30% L	70	30	0.60

Testing methods. The microstructure and hydration of the limestone-filled pastes were studied with a scanning electron microscope (SEM). Energy dispersive X-ray microanalysis (EDXA) was carried out to determine the elemental composition of the mineral phases in the matrix and at interfaces. Specimen fragments were taken from the curing chamber at 7, 28 and 35 days. EDXA analysis was carried out using a detector at 20KV. The images were captured between 2 and 10KV. The mineralogical composition of the NHL5 was analysed by X-Ray Diffraction (XRD), using a Phillips PW1720 XRD with a PW1050/80 goniometer and a PW3313/20 Cu k-alpha anode tube at 40kV and 20mA. All measurements were taken between 3 and 60 degrees (2θ) at a step size of 0.02

degrees/second. The porosity was tested according to RILEM recommendations [40]. The water absorption was measured according to UNE [41] and the capillary suction estimated with the EN 1925 procedure [42]. The water vapour permeability was measured with the wet cup method in EN 1015-19 [43]. The test lasted for 8 weeks and the samples were weighted at weekly intervals. The weight stabilised during the first week and the subsequent 7 weeks of readings allowed to determine the water vapour coefficient. The compressive and flexural strengths were measured according to EN 1015-11 [43]. The flexural test was performed on 40x40x160 mm specimens using rates of loading of 1 mm/min. The compressive strength was measured on the half prisms at the same loading rate.

Results and discussion

The limestone / hydraulic lime system

While limestone reactions are well documented in PC, the system limestone-HL has not yet been investigated in detail. NHL5 typically contains more free lime and residual CaCO_3 than PC [38, 44, 45] (Table 4). Furthermore, due to the different production temperature (<1200°C for NHL5 vs >1300°C in PC), the calcium silicate, aluminate and ferrite contents are different. In PC, alite is the most abundant component and aluminates and aluminoferrites are usually present (c.10%) while in NHL5, belite is the most abundant and aluminate and ferrites are very low (Table 4). Alite hydrates quickly, being the main contributor to early strength and partially responsible for the early set but belite hydrates late (after c. 18 hours [46]) and contributes little to strength [47]. When alite hydrates C-S-H forms together with a supersaturated solution from which CH crystals subsequently precipitate. Belite progresses likewise, however at a slower pace and producing 2/3rd less CH [48-49].

Table 4. Comparison of mineral composition of NHL5 and cement [38, 44, 45].

Compounds	NHL5- % by mass	CEM I- % by mass
Insoluble content	4 - 5.6	trace
Free lime - Ca(OH)_2	21 - 22	2
Unburnt Ca CO_3	23	0
Alite – C_3S	Trace - 2	58
Belite - C_2S	43 - 45	13
Tricalcium aluminate - C_3A	0.7 - 2	9
Gehlenite - C_2AS	1.3 - 2	0
Ca aluminoferrite - C_4AF	0.7 - 2	8
Gypsum - $\text{CaSO}_4 \times 2\text{H}_2\text{O}$	Trace - 0.7	5

The reactions between limestone and alite/aluminates are widely acknowledged in PC however, rather than alite, the NHL5 contains significant belite (43%) and little aluminate (0.7-2%) - table 2. In spite of this, given their similar composition and hydration kinetics of alite and belite, it is likely limestone also affects belite hydration. Furthermore, limestone is reported to react with cement containing no aluminates: Monteiro and Meht [50] observed the formation of a $\text{CaCO}_3 / \text{Ca}(\text{OH})_2$ compound at interfaces that strengthens the transition zone due to the substitution of the large and highly oriented CH crystals with the $\text{CaCO}_3\text{-Ca}(\text{OH})_2$ compound of lower crystallinity.

Effect of limestone filler on the strength of NHL5 mortar

All the limestone-filled mortars reached their maximum compressive strength at 90 days to later drop while the NHL5 mortar continued to develop strength, increasing by c.14 between 90 and 180 days (figure 5). This strength will further grow up to one or two years. The compressive strength of standard NHL5 mixes usually multiplies by 4-5 times between 28 days and one year and keeps growing by c. 10% between 1 and 2 years [13, 38, 51]. The 10 and 20% limestone replacements enhanced the 28-day compressive strength of the NHL5 by 36 and 20% respectively while the 30% limestone lowers it considerably (Figure 5). The 10% limestone mortar's strength remains superior up to 180 days. After this, the NHL5 mortar starts to become stronger. The strength of the 20% limestone mortar remains superior up to 125 days; later (180 days) is c.14% lower than the NHL5. The 30% replacement decreased the compressive strength of the NHL5 mortar at all ages (by 25-59%). PC authors report strength loses for 15-25% limestone replacement and over [30-31]. The early strength increase caused by the limestone is attributed to the lower water demand of the limestone-filled mortars; the increase of early hydrates and their placement.

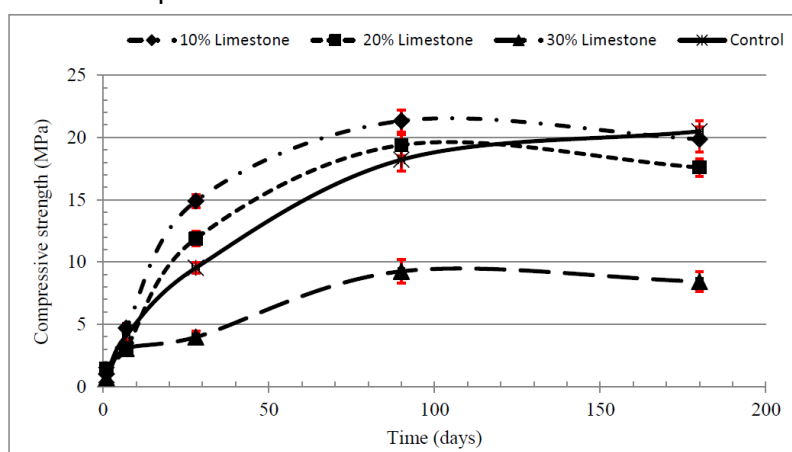


Figure 5. Compressive strength of NHL5 and NHL5-limestone-filled mortars over 180 days. COV 10% limestone=3-15%; 20% limestone=3-8%; 30% limestone 1-12%; 100%NHL5=4-14.

The mortars reached their maximum flexural strength at 90 days to later drop. This drop is usually attributed to the transformation of early hydrates into more stable, weaker phases [34]. The 10% replacement significantly increased the flexural strength of the NHL5 by 56% at 28 days (Figure 6). It enhanced the NHL5 flexural strength up to c.100 days, after this time, it begins to drop (Figure 6). The flexural strength of the 20% limestone mortar is marginally superior up to 28 days however, at 90 and 180 days, it is 20 and 34% lower (respectively) than the NHL5 mortar. These differences will become more pronounced as the flexural strength of the NHL5 will rise by c.16% or over between 180 days and 1 year [51]. The 30% limestone replacement reduced the NHL5 flexural strength at all ages however much less than the compressive strength.

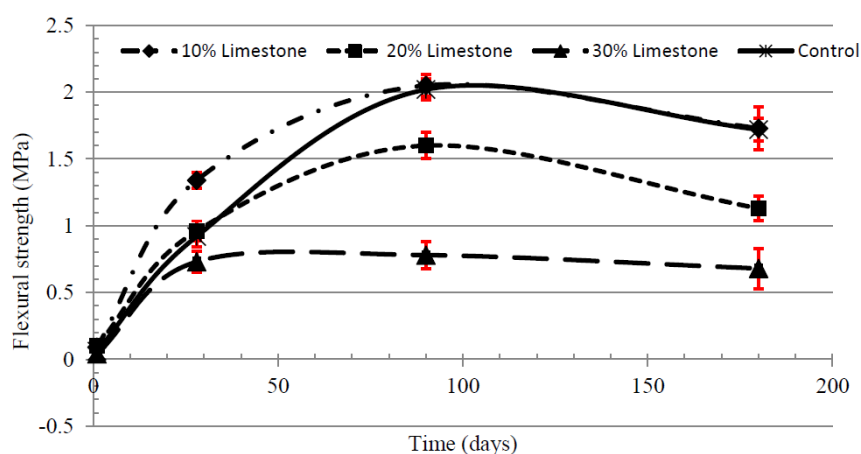


Figure 6. Flexural strength development of NHL5 and NHL5-limestone-filled mortars. COV 10% limestone=4-12%; 20% limestone=4-7%; 30% limestone 0-15%; 100%NHL5=0-7%.

Effect of limestone filler on NHL5 hydration

The SEM/EDXA analyses evidenced that the limestone particles are active on hydration, as they are often covered with hydrates even after 7 days of curing. The limestone changes the microstructure of the hydraulic lime paste and the nature of some of the hydration phases. The NHL5 paste shows more uniformly distributed C-S-H fibrils and gels (figure 7) whereas in the limestone-filled pastes, particles covered with hydrate fibrils (probably C-S-H) are abundant (figure 8). The 10% limestone filled pastes at 7 days show limestone particles and occasional hydrates (fibrils-probably C-S-H) and hexagonal plates). At 28 days, extensive fibrous hydrates alternating with occasional plates cover most particles (figure 8). The 30% limestone pastes, at 7 and 28 days, show plentiful products of hydration similar to those in the 10% pastes, with abundant hexagonal plates and fibril-coated particles. Figure 9 shows a calcium silicate, possibly belite (figure 10) covered with hydrates including plates and smaller crystals. The elemental analysis of the larger plates (figure 11), often hexagonal, suggest that they are CaCO_3 / $\text{Ca}(\text{OH})_2$ compounds formed by the reaction between the limestone (CaCO_3) and the C_2S –belite. As aforementioned, Monteiro and Meht [50] observed the formation of a CaCO_3 / $\text{Ca}(\text{OH})_2$ compound at interfaces leading to the strengthening of the transition zone. In

the limestone-filled pastes, hexagonal and planar plates, similar in morphology to CH but often of lower-crystallinity often appear as products of hydration (figures 8-9) on particle interfaces and in the paste. Their spectra always show Si, Al and a raised C peak suggesting that they can be hydrates resulting from the limestone reaction.

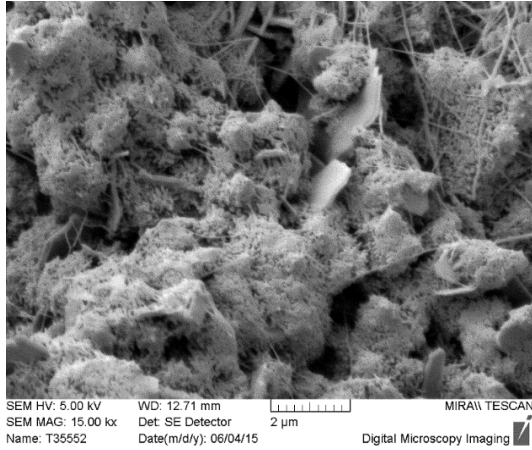


Figure 7. NHL5 paste at 28 days shows C-S-H evenly spread and hexagonal aluminosilicate hydrates.

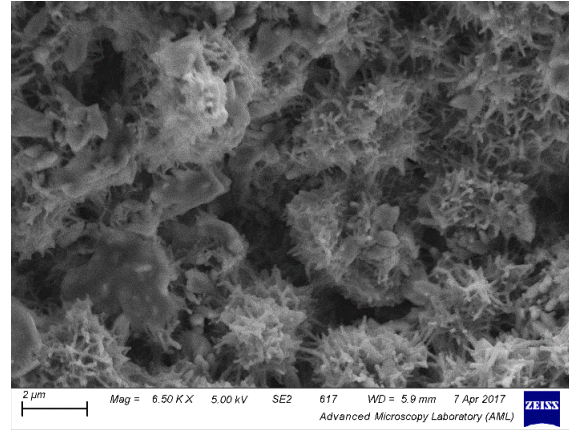


Figure 8. 10% limestone-filled paste at 28 days showing hydrates covering most particles.

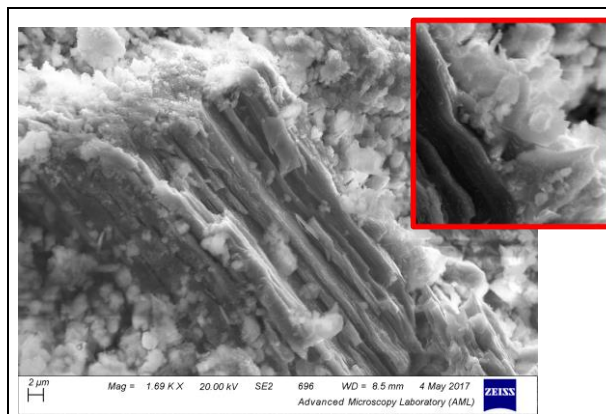


Figure 9. Calcium silicate clinker in a 30% limestone-filled paste with abundant plates (tending to hexagonal) and lower crystallinity phases at the interface. Insert: Detail of interface with hydrate plates. Field of view c. 8 μm.

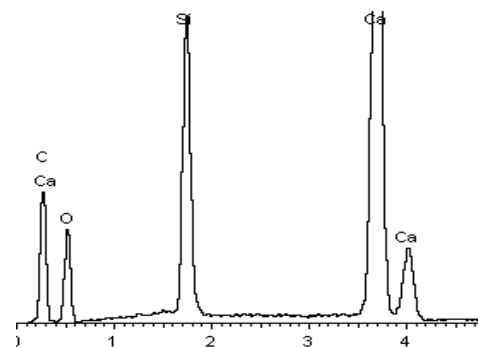


Figure 10. Elemental composition of the calcium silicate in figure 9- probably belite.

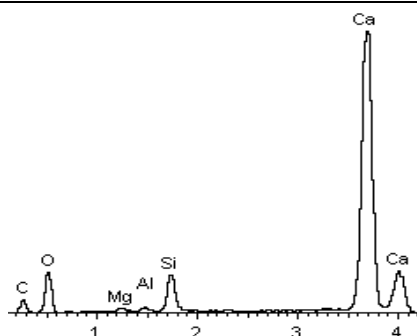


Figure 11. The elemental composition of the larger plates at the interface (figure 9) suggest that they are CaCO_3 / $\text{Ca}(\text{OH})_2$ compounds formed by the reaction between the limestone (CaCO_3) and the C_2S –belite.

Effect of limestone filler on the hygric properties of NHL5 mortar

The 10 and 20% limestone replacements slightly reduced the porosity of the NHL 5 mortar by c. 8 and 5% respectively while the 30% replacement increased it by 12%. A similar trend was observed for water absorption (figure 12), as this property strongly relates to the open porosity. The 10 and 20% limestone replacements decreased water absorption by 9 and 7% respectively while the 30% replacement raised it by c.14%.

The results agree with PC authors: Cussino and Negro [34] experimentally confirmed a decrease in porosity as calcium carboaluminate hydrate was formed. Similarly, according to Tsvilis et al. [52, 53], 10% limestone (at 0.50 w/c and 3:1 sand:cement) decreased the porosity of PC materials while replacements over 20% increased it. PC authors usually attribute this reduction to the additional nucleation sites (provided by the limestone particles) which result in a further distribution of C-S-H blocking capillary pores. A refinement of the pore structure due to the limestone reaction has even been reported in low aluminate and ferrite cement [54]. The porosity decrease can also relate to the well-known physical effect of fillers increasing packing and enhancing density.

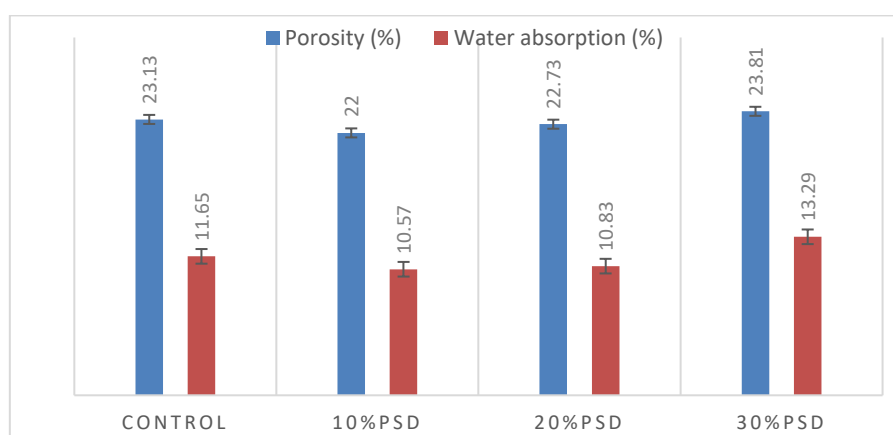


Figure 12. Porosity and water absorption of NHL5 and NHL5/limestone mortars at 90 days. COVs=0.10-3.20. PSD= Portland Stone dust.

Capillary suction followed a similar trend. The suction of the 10% limestone mortar is the lowest (30% lower than the NHL5 mortar-figure 13). The 20% limestone shows a 9% decrease in suction while the 30% mortar shows the highest capillarity, 73% over the NHL5 despite having similar porosity. Suction is determined by pore size and interconnection, it seems that beyond the 20% replacement, limestone significantly increases capillary suction which may be due to the more abundant interfaces rising the quantity of suction-active pores. The slightly lower hygric properties of the 10 and 20% limestone replacements can be partly due to their lower water demand however, the water content of the 30% replacement is even lower (W/B=0.6 vs W/B=0.7 for the 10% replacement) and yet, the composites show greater porosity and permeability which

may be due to the presence of more abundant interfaces. The coefficient of variation (COV) indicates reliable values.

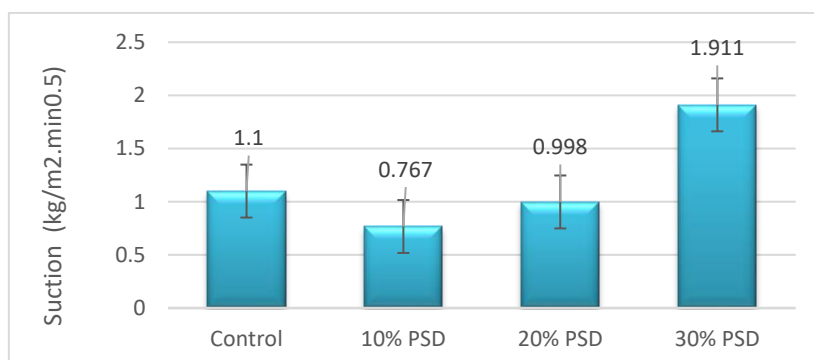


Figure 13. Capillary suction of of NHL5 and NHL5/limestone mortars at 90 days. COV=1.14 (control); COV=6.40 (10-20%); COV=8.19 (30%).

The 10 and 20% limestone replacements slightly lowered the water vapour permeability of the NHL5 mortars while the 30% replacement slightly enhanced it (figure 14) however, the variation is not significant. Water vapour permeability is determined by the finest pores (<75µm in rocks [55]). Therefore, the limestone replacement preserves the finest pores in the mortars while lowering the water-transport active pores.

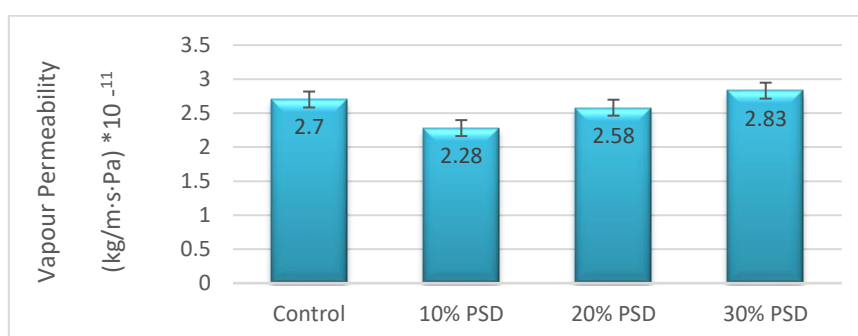


Figure 14. Water vapour permeability of NHL5 and NHL5/limestone mortars at 90 days. COV=8 (control); COV=3-8 (10-20%); COV=6 (30%).

Conclusion

This paper replaces NHL5 mortar binder with limestone in an effort to lower high ultimate strengths that can be detrimental for certain fabrics. The hydration of NHL5 in the presence of limestone and the impact on mortar properties are studied.

Despite the lime's low aluminate content, limestone reaction is evident. The limestone changes the microstructure of the NHL5 paste and the nature of some hydrates. Limestone particles covered with C-S-H fibrils are abundant at early stages. Hydrate plates (probably CaCO₃/Ca(OH)₂ compounds formed by limestone-belite reaction) strengthen transition zones. Calcium carbo-silicate and carbo-aluminate hydrates were evidenced in the matrix as plates, similar to CH but often of lower-crystallinity. The

limestone fineness ($63\% < 63 \mu\text{m}$), its permeability and the significant specific surface area of its microcrystalline carbonate components have probably enhanced reactivity. When NHL5 is replaced with 10-30% limestone, the finest mortar pores are preserved (water vapour permeability varies insignificantly) whereas the water-transport active pores tend to slightly decrease (with $<20\%$ limestone) or increase (at 30% replacement). The 10% replacement reduced porosity, water absorption and capillary suction by 8, 9 and 30% respectively; and the 20% replacement by 5, 7 and 9%. In contrast, the 30% replacement increased the properties by 12, 14 and 73% respectively. The strong capillary suction rise is likely due to the more abundant interfaces of the 30% replacement rising the quantity of suction-active pores. The reduction of hygric properties at 10-20% replacement is likely due to additional, limestone-induced hydrates.

The 10-20% limestone replacements increased the 28-day strength. However, the limestone lowered strength after 90 days (flexural) or 180 days (compressive) while the NHL5 mortar continued to develop compressive strength, increasing by c.14 between 90 and 180 days and a further c. 10% between 180 days and 1 year. The reduction of the late strength caused by the limestone can be due to transformation (e.g. carbonation) of some limestone-induced hydrates such as the $\text{CaCO}_3/\text{Ca}(\text{OH})_2$ compounds or even the calcium carbo-silicate and carboaluminates hydrates.

Contrary to PC, the limestone lowers the water demand of the NHL5 mortars increasing 28-day strength but lowering the final strength without a major effect on moisture transport and vapour permeability. To achieve a proper workability using less water in mortars has benefits relevant for those involved in mortar design.

A NHL mortar's water content can be lowered by partially replacing the binder with limestone. This would increase strength for up to 125-180 days however, after this, the limestone would lower the strength of the NHL5. The limestone can lower the strength of NHL5 so that they do not become overly strong over long time periods and damage some historic fabrics.

Acknowledgment

This research was funded by the Irish Research Council. Testing was carried out in the Dept. of Civil Engineering, Trinity College Dublin. We thank Chief Technician D. McAuley for facilitating our work and M. Grimes and E. Dunne for their assistance. Thanks to Dr R. Goodhue of the ICRAAG (Irish Centre for Research in Applied Geosciences) for his help with the XRD analysis and to D. Simpson and C. Dooley of the ICRAAG and the Advanced Microscopy Laboratory (SFI supported centre at the AMBER, CRANN Institute) respectively for their help with the SEM.

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